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# COLLABORATIVE RESEARCH AND DEVELOPMENT (CR&D)

## Delivery Order 0070: Ab-initio Modeling of Slippery Hexagonal Solids

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**Universal Technology Corporation**

**MAY 2008**
**Final Report**



**AIR FORCE RESEARCH LABORATORY**
**MATERIALS AND MANUFACTURING DIRECTORATE**
**WRIGHT-PATTERSON AIR FORCE BASE, OH 45433-7750**
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**UNITED STATES AIR FORCE**

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**14. ABSTRACT**
This research in support of the Air Force Research Laboratory Materials and Manufacturing Directorate was conducted at Wright-Patterson AFB, Ohio from 18 April 2007 through 17 March 2008. This task worked to develop, validate, and explore the models of slippery hexagonal lattice solids using ab initio density function theory (DFT) calculations. The various mechanical, electronic, and other properties of the following hexagonal slippery solids were evaluated: Lattice constants, a, c; Elastic Constants, C11, C12, C33, C44, C13, C66L; Density of States (DOS); Local Density of States (LDOS); Band Structures; Voigt, Reuss, Hill Bulk Moduli, Bv, Br, Bh; Voight, Reuss, Hill Shear Moduli, Gv, Gr, Gh; Poisson's Ratio σ; Young's Modulus, E; and Relationships with Coefficient of friction, u. The results are shown in appropriate tables.

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TO UTC and WPAFB
FROM Sanjay V. Khare
DATE April 18, 2008

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The electronic properties of remaining compounds i.e., $MoX_2$, where (X = O, S, Se, Te) were found in the first two weeks. Their band structures, local density of states and total density of states were plotted and studied. A comparative study of all the four compounds $MoO_2$, $MoS_2$, $MoSe_2$, and $MoTe_2$ in the group was done.

Meanwhile, literature survey was performed to find a relationship between the elastic constants and the coefficient of friction. Preliminary studies showed that there exists a relationship between coefficient of friction and Young's modulus. Further studies were carried out in that direction.

After completion of the computations for the mechanical and electronic properties of 'Mo' compounds along $16^{th}$ group of the periodic table, we searched for other materials of interest to the Air Force. We then found published work by Dr. Voevodin of the Wright Patterson Air Force Base (WPAFB) on $NbSe_2$ which had similar tribological behavior to $MoX_2$. We thus began working on $NbX_2$ by the end of the last week.

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As in case of Mo, we decided to run through the $16^{th}$ group i.e., O, S, Se, and Te for a systematic comparison of properties. Hence we considered compounds with identical structures such as $NbO_2$, $NbS_2$, $NbSe_2$ and $NbTe_2$.

The first two weeks were consumed in conducting various convergence tests on the above mentioned compounds of Nb. The same procedure as in case of $MoX_2$ was followed to find lattice constants 'a' and 'c' i.e., by keeping one of them constant and varying the other. Like in case of $NbSe_2$, initially 'c' was fixed and 'a' was varied and then 'a' was fixed (fixed to the value found previously) and 'c' was varied. Similar procedures were followed for $NbTe_2$ and both showed a consistent pattern in reaching convergence. Repeating this process for $NbO_2$ and $NbS_2$ yielded their lattice constants 'a' and 'c'.

After the lattice constants were found, the independent parameter 'u' was taken into consideration. Few more tests were conducted with varying 'u' and fixed 'a' and 'c' to see to it that the independent parameter 'u' was also finalized.

Elastic constants were found for all the four compounds. All the five independent elastic constants for $NbO_2$, $NbS_2$, $NbSe_2$ and $NbTe_2$ were calculated. Bulk modulus was also

found from these elastic constants from the relationship between elastic constants and bulk modulus derived previously.

Simultaneously further studies were made on the relationship between coefficient of friction and elastic constants. This time it was clearly found that the coefficient of friction is directly proportional to shear strength and inversely proportional to effective Young's modulus raised to two third.

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Now since the mechanical properties of the materials were calculated, work was started on calculating the electronic properties of the materials $NbO_2$, $NbS_2$, $NbSe_2$ and $NbTe_2$. The band structures, local density of states and total density of states of $NbX_2$ were plotted and the required values were found from these plots. As in case of the 'Mo' series, the first Brillouin zone of a hexagonal lattice was chosen, and the high symmetry k points along this region were marked. These k-points along with other files were used to plot band structures. All the results were plotted and compared. By the end of the month work on $NbX_2$ was completed.

Literature survey revealed that 'W' was the next material of interest for comparison with 'Mo' and 'Nb' series. Hence, we started working on the $WX_2$ series next. To start with, the 'a' and 'c' values of all the four materials $WO_2$, $WS_2$, $WSe_2$ and $WTe_2$ were evaluated.

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We proceeded to compute the elastic constants and other mechanical properties i.e., Bulk modulus, Young's modulus, Poisson's ratio and others. We followed this by finding the electronic properties of the $WX_2$. The band structures were estimated using the k-points derived from the first Brillouin zone of the hexagonal lattice as in case of other compounds. Also the local density of states and total density of states were plotted and compared.

At last a comparative study of all the compounds researched so far i.e., $MoX_2$, $NbX_2$, $WX_2$ (X = O, S, Se, Te) was done. Also by the end of the grant period an equation was derived for the relationship between elastic constants and coefficient of friction and was checked for authenticity.

RE Beyond the grant period

We are planning to closely compare our theoretical results with experimental results obtained at WPAFB. We are closely collaborating with WPAFB scientists led by Dr. Andrey Voevodin and working on journal publications of these results.

TO UTC and WPAFB
FROM Sanjay V. Khare
DATE May 21, 2008

RE Final report for Collaborative Research and Development (CR&D) Task Order 0070

In the course of our effort we evaluated various mechanical, electronic and other properties of several hexagonal slippery solids which were listed below:

1. Lattice constants, a, c.
2. Elastic Constants, $C_{11}$, $C_{12}$, $C_{33}$, $C_{44}$, $C_{13}$, $C_{66}$.
3. Density of States (DOS).
4. Local Density of States (LDOS).
5. Band Structures.
6. Voigt, Reuss, Hill Bulk Moduli, $B_v$, $B_r$, $B_h$.
7. Voigt, Reuss, Hill Shear Moduli, $G_v$, $G_r$, $G_h$.
8. Poisson's Ratio, $\sigma$.
9. Young's Modulus, E.
10. Relationship with Coefficient of friction, u.

We also derived a relationship between shear strength, Young's modulus and coefficient of friction. It was found that coefficient of friction is directly proportional to the shear strength and inversely proportional to the effective Young's modulus raised to the power of one third.

Listed in Tables 1-3 are the results of our computations. Table 1 lists properties of $MoX_2$ (X = O, S, Se, Te).

**Table 1a: The five independent elastic constants ($C_{11}$, $C_{12}$, $C_{33}$, $C_{44}$, $C_{13}$), Bulk Modulus (B), lattice constants (a and c) and Energy band gap ($E_g$).**

| | $MoO_2$ | $MoS_2$ | $MoSe_2$ | $MoTe_2$ |
|---|---|---|---|---|
| $C_{11}$ (GPa) | 494.218 | 231.006 | 195.705 | 140.080 |
| $C_{12}$ (GPa) | 184.942 | 65.374 | 46.465 | 38.480 |
| $C_{33}$ (GPa) | 44.950 | 48.342 | 52.748 | 53.388 |
| $C_{44}$ (GPa) | 6.528 | 17.439 | 20.068 | 25.613 |
| $C_{13}$ (GPa) | 12.318 | 10.235 | 14.818 | 15.908 |
| B (GPa) | 161.393 | 75.782 | 66.262 | 52.682 |

| | | | | |
|---|---|---|---|---|
| **a** (Å) | 2.799 | 3.123 | 3.250 | 3.472 |
| **c** (Å) | 9.856 | 12.190 | 12.750 | 13.762 |
| $E_g$ (eV) | 0.514 | 0.758 | 0.692 | 0.659 |

**Table 1b: The Voigt Bulk Modulus ($B_v$), Voigt Shear Modulus ($G_v$), Reuss Bulk Modulus ($B_r$), Reuss Shear Modulus ($G_r$), Hill Bulk Modulus ($B_h$), Hill Shear Modulus ($G_h$), Young's Modulus (E) (all in units of GPa), Poisson's Ratio ($\sigma$), and relationship $u = G_h / E^{2/3}$ (in units of $(GPa)^{1/3}$)which is a quantity proportional to the coefficient of friction.**

| | $B_v$ | $G_v$ | $B_r$ | $G_r$ | $B_h$ | $G_h$ | $\sigma$ | E | u |
|---|---|---|---|---|---|---|---|---|---|
| $MoO_2$ | 161.393 | 88.459 | 41.991 | 14.231 | 101.692 | 51.345 | 0.284 | 131.846 | 1.982 |
| $MoS_2$ | 75.782 | 51.840 | 40.094 | 29.233 | 57.938 | 40.536 | 0.216 | 98.611 | 1.899 |
| $MoSe_2$ | 66.262 | 47.488 | 42.771 | 31.507 | 54.517 | 39.498 | 0.208 | 95.443 | 1.891 |
| $MoTe_2$ | 52.682 | 37.955 | 40.716 | 32.793 | 46.699 | 35.374 | 0.198 | 84.728 | 1.834 |

Table 2 lists the properties of $NbX_2$ (X = O, S, Se, Te).

**Table 2a: Same properties as in Table 1a for $NbX_2$ (where X = O, S, Se, Te).**
**Note:** ' – ' indicates negative value which is unphysical, i.e. the compound is unstable.

| | $NbO_2$ | $NbS_2$ | $NbSe_2$ | $NbTe_2$ |
|---|---|---|---|---|
| $C_{11}$ (GPa) | 421.003 | 190.870 | 155.590 | 89.290 |
| $C_{12}$ (GPa) | 216.367 | 62.630 | 41.510 | 45.610 |
| $C_{33}$ (GPa) | 53.892 | 54.360 | 62.140 | 74.560 |
| $C_{44}$ (GPa) | 18.960 | 1.550 | - | 11.140 |
| $C_{13}$ (GPa) | 35.037 | 14.260 | 15.515 | 14.760 |
| **B** (GPa) | 163.198 | 68.711 | 57.600 | 44.822 |
| **a** (Å) | 2.948 | 3.285 | 3.387 | 3.576 |

| | | | | |
|---|---|---|---|---|
| c (Å) | 9.179 | 11.901 | 12.545 | 13.583 |
| $E_g$ (eV) | 0.453 | 0.758 | 0.692 | 0.494 |

**Table 2b: Same properties as in Table 1b for $NbX_2$ (where X = O, S, Se, Te).**
**Note:** ' – ' indicates negative value which is unphysical, i.e. the compound is unstable.

| | $B_v$ | $G_v$ | $B_r$ | $G_r$ | $B_h$ | $G_h$ | σ | E | u |
|---|---|---|---|---|---|---|---|---|---|
| $NbO_2$ | 163.198 | 68.678 | 52.717 | 32.106 | 107.957 | 50.392 | 0.298 | 130.821 | 1.955 |
| $NbS_2$ | 68.711 | 36.441 | 43.822 | 3.697 | 56.267 | 20.069 | 0.341 | 53.809 | 1.408 |
| $NbSe_2$ | 57.600 | - | 45.374 | - | 51.487 | - | - | - | - |
| $NbTe_2$ | 44.822 | 20.691 | 42.770 | 16.719 | 43.796 | 18.705 | 0.313 | 49.122 | 1.395 |

Table 3 lists the properties of $WX_2$ (X = O, S, Se, Te).

**Table 3a: Same properties as in Table 1a for $WX_2$ (where X = O, S, Se, Te).**

| | $WO_2$ | $WS_2$ | $WSe_2$ | $WTe_2$ |
|---|---|---|---|---|
| $C_{11}$ (GPa) | 566.410 | 259.473 | 214.172 | 151.926 |
| $C_{12}$ (GPa) | 190.180 | 59.057 | 41.988 | 28.554 |
| $C_{33}$ (GPa) | 47.840 | 47.640 | 54.118 | 53.984 |
| $C_{44}$ (GPa) | 10.727 | 18.876 | 21.415 | 26.677 |
| $C_{13}$ (GPa) | 11.145 | 14.337 | 13.906 | 15.029 |
| B (GPa) | 178.400 | 82.449 | 69.118 | 52.784 |
| a (Å) | 2.793 | 3.123 | 3.245 | 3.470 |
| c (Å) | 9.890 | 12.201 | 12.806 | 13.825 |
| $E_g$ (eV) | 0.923 | 0.900 | 0.824 | 0.791 |

**Table 3b: Same properties as in Table 1b for $WX_2$ (where X = O, S, Se, Te).**

| | $B_v$ | $G_v$ | $B_r$ | $G_r$ | $B_h$ | $G_h$ | σ | E | u |
|---|---|---|---|---|---|---|---|---|---|
| $WO_2$ | 178.400 | 106.460 | 44.506 | 22.041 | 111.453 | 64.250 | 0.258 | 161.682 | 2.165 |
| $WS_2$ | 82.450 | 59.516 | 41.417 | 31.364 | 61.934 | 45.440 | 0.205 | 109.532 | 1.985 |
| $WSe_2$ | 69.118 | 53.295 | 43.644 | 33.922 | 56.381 | 43.609 | 0.193 | 104.010 | 1.972 |
| $WTe_2$ | 52.784 | 42.956 | 40.692 | 35.341 | 46.738 | 39.149 | 0.173 | 91.811 | 1.924 |

We are planning to closely compare our theoretical results with experimental results obtained at WPAFB. We are closely collaborating with WPAFB scientists led by Dr. Andrey Voevodin and working on journal publications of these results.